

FORM PTO-1390 (Modified)
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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

14506

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

09/807662

INTERNATIONAL APPLICATION NO.

PCT/EP99/07848

INTERNATIONAL FILING DATE

15 October 1999 (15.10.99)

PRIORITY DATE CLAIMED

15 October 1998 (15.10.98)

TITLE OF INVENTION

POLYAMIDE COMPOSITION, STABILIZED WITH COPPER SALT AND AROMATIC HALOGEN
COMPOUNDS

APPLICANT(S) FOR DO/EO/US

Klaus Titzschkau

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/ISA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Assignee: L. Bruggemann KG
Heilbronn, Germany

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) 097807662		INTERNATIONAL APPLICATION NO. PCT/EP99/07848		ATTORNEY'S DOCKET NUMBER 14506	
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24. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :			CALCULATIONS PTO USE ONLY	
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	\$1000.00			
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	\$860.00			
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$710.00			
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	\$690.00			
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	\$100.00			
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$860.00		
Surcharge of \$130.00 for furnishing the oath or declaration later than _____ months from the earliest claimed priority date (37 CFR 1.492 (e)).		<input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30		\$130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	13 - 20 =	0	x \$18.00		\$0.00
Independent claims	3 - 3 =	0	x \$80.00		\$0.00
Multiple Dependent Claims (check if applicable) <input checked="" type="checkbox"/>					\$270.00
TOTAL OF ABOVE CALCULATIONS =					\$1,260.00

☐ Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.

SUBTOTAL =				\$1,260.00	
Processing fee of \$130.00 for furnishing the English translation later than _____ months from the earliest claimed priority date (37 CFR 1.492 (f)).				<input type="checkbox"/> 20 <input type="checkbox"/> 30	\$0.00
TOTAL NATIONAL FEE =				\$1,260.00	

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐

TOTAL FEES ENCLOSED =				\$1,260.00	
				Amount to be: refunded	\$
				charged	\$

a. ☒ A check in the amount of **\$1,260.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **19-1013/SSMP**. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Leopold Presser
SCULLY, SCOTT, MURPHY & PRESSER
 400 Garden City Plaza
 Garden City, NY 11530
 (516) 742-4343

SIGNATURE

Leopold Presser

NAME

19,827

REGISTRATION NUMBER

April 16, 2001

DATE

**Polyamide composition, stabilized with copper salt and aromatic
halogen compounds**

The present invention relates to stabilized polyamide compositions.

Polymers are degraded easily when heated by oxidation, which leads to embrittlement of the material and to mechanical failure of the products produced therefrom. Therefore particular chemical compounds are added which can delay the time of embrittlement with different activity. These so-called antioxidants are mostly built on the basis of phenyl derivatives, amine derivatives or phosphorous derivatives. Specific variants of antioxidants are employed with polyamides. One in particular active class of compounds, which does not have any activity with other polymers, are the so-called copper stabilizers.

These types of stabilizing systems are long known and are used widely for the preparation of polyamides, for examples for polyamide filaments which are used for the production of tyre cord and for polyamide extrusion molding parts for technical employment, in particular in the area of technical engineering (automobiles) and the electronic industry (switches, printed circuit boards).

These copper stabilizers usually consist of two component. As first component a compound such as copper halide or other copper salts are employed. In order to be effective as antioxidants, as second component a halogen compound must be added in a large surplus. Used in this respect are in particular potassium iodide and also potassium bromide. The employed molar ratio of copper to halogen is typically 1:5-15. The recommended amount is generally 30 to 200 ppm copper and accordingly 150 to 3,000 ppm halogen.

These copper stabilizers do show somewhat satisfying results with polyamides.

However, these commonly employed copper stabilizers do show some severe drawbacks.

Polyamides take up (conditioning) approximately 3% water. If the temperature changes water soluble components are extracted from the polyamide to the surface, which leads to the formation of scale. If copper halides, potassium halides or other soluble halides are employed these will be extracted to the surface and will form a hygroscopic scale which will react mostly acidic. Therefore the tracking resistance will decrease. With electric components this may lead to failure. If contact with metals is given the contact places will endure increased corrosion. Requirements of the electronic industry and the automobile industry regarding the question of tracking resistance are therefore difficult to fulfil.

At the same time these stabilizers are difficult to disperse in the polyamide. When preparing stabilized polyamides it is important to make sure that the employed stabilizers are finely powdered and can be admixed with the polyamide very homogeneously. One problem associated therewith is usually the tendency of the usually employed components to agglomerate. The raw materials must therefore be ground very finely and must be protected against reagglomeration. The addition itself is usually very difficult to control, therefore usually a master batch will be produced which will be added. Even then such a heterogeneous mixture of solid particles in a melt is never optimal, compared with the hypothetical case that the stabilizer itself would be meltable and could be dispersed homogeneously under working conditions, as is the case with phenolic, amine and other antioxidants. The crystalline particles of the stabilizer salts effect the physical properties of the polyamides negative, even if they are finely dispersed. This does not only result from possible inhomogeneity but also from the fact that fine particles act as crystallisation nuclei which result in a higher crystallinity in polymers. This can lead to negative side effects. The impact strength can for example decrease by 20 to 30%, compared with the initial value of the non-stabilized polyamide.

Usual stabilizing compounds furthermore lead in polyamides after conditioning often to a bluish or greenish discoloration. Polyamides reinforced with fiber glass may furthermore show a brown coloration due to the formation of copper oxide, resulting from high sheer stress given during processing. In particular negative are variations of the discoloration during the production cycles, which will make the use of the produced materials for non-colored or colored products difficult. Therefore such polyamides are usually employed after black coloration.

Usual stabilizing compounds are often added during the polymerization as aqueous solution in order to optimise the dispersion. One drawback is however that this addition may lead to formation of scale of metallic copper or of copper oxide on the metal surface of the employed vessels and melt extruders. This may lead to variation in coloration and therefore to the discontinuation of the production. During spinning of filaments scale formation at the nozzle is often encountered which will lead to the discontinuation of the process.

In view of these drawbacks several improvements were proposed.

EP-A-390277 discloses a stabilized polyamide 4.6 composition. This particular high melting point polyamide can be stabilized by addition of an insoluble copper salt and a halogen substituted organic compound. These compositions are suitable for electric or electronic uses.

GB-A-1131933 and GB-A-1143826 disclose stabilized linear polyamides, stabilized with a mixture of a copper compound, soluble in the polyamide, and a specific halogen containing organic aliphatic compound with at most 7 carbon atoms. These organic compounds have however a high volatility. This may lead to undesired embrittlement of the material due to flow out of the organic compound.

Starting from the above described problems associated with the prior art it is therefore the object of the present invention to provide a stabilized polyamide composition which does not show the above named drawbacks, while simultaneously improving the long term temperature stability.

This object is solved in accordance with the present invention by the provision of a stabilized polyamide composition, characterized in that as stabilizer at least one copper salt and at least one organic halogen containing compound is contained, selected among the group consisting of (a) aromatic compounds ; (b) aliphatic phosphates; (c) paraffins; or mixtures thereof, with the proviso that if the aromatic compound is a bromine containing styrene oligomer the polyamide is not polyamide 4.6.

Surprisingly it was found that such stabilized polyamide compositions do show improved properties and an increased long term temperature stability.

Furthermore the present invention provides a process for the preparation of a stabilized polyamide composition, comprising the mixing of at least one polyamide, at least one copper salt and at least one organic halogen containing compound selected among the group consisting of (a) aromatic compounds ; (b) aliphatic phosphates; (c) paraffins; or mixtures thereof, with the proviso that if the aromatic compound is a bromine containing styrene oligomer the polyamide is not polyamide 4.6.

Furthermore the present invention provides the use of at least one copper salt and at least one organic halogen containing compound, defined as given above, for the stabilization of polyamide compositions.

Preferred are each time compounds (a) and/or (b).

The at least one polyamide in accordance with the present invention may be any polyamide. Polyamides are polymers showing recurrent carbon amide groups $-\text{CO}-\text{NH}-$ in the polymer backbone. Polyamides are made from

- (a) amino carboxylic acids and their functional derivatives, for example lactames; or from
- (b) diamines and dicarboxylic acids or their functional derivatives.

By varying the monomer units polyamides are obtainable in a broad variety. In accordance with the present invention all polyamides may be stabilized, for example copolyamides or homopolyamides. Usable are furthermore block copolymers of polyamides and polyethers and other polymer modified polyamides. The most common types are polyamide 6 from ϵ -caprolactam and polyamide 66 from hexamethylene diamine and adipic acid. Other important polyamides are polyamide 610, polyamide 11, polyamide 12, PACM-12, MPB-I, PPD-T and the aramides.

It is furthermore possible to use blends of polyamides with other polymers. However, the stabilizing compounds may exert negative effects with respect to the blend components. Therefore these must be chosen carefully.

In accordance with the present invention any copper salts may be used.

Preferred are salts of mono- or divalent copper with inorganic or organic acids. Examples of suitable copper salts are copper (I) salts, such as CuI , CuCl , or CuCN , copper (II) salts, such as CuCl_2 , CuBr_2 , Cu-acetate, Cu-sulfate, Cu-stearate, Cu-propionate, Cu-butyrate, Cu-lactate, Cu-benzoate or Cu-nitrate, as well as ammonium complexes of the above given salts.

Furthermore compounds such as Cu-acetylacetonate or Cu-EDTA may be employed. It is furthermore possible to use mixtures of different copper salts. Optional Cu powder may be used. This reacts with polyamide melts under formation of copper compounds. Preferred are Cu (I) halides and Cu-salts of organic acids, in particular preferred are CuI and Cu-acetate.

The amount of copper, used in the stabilized polyamide compositions is not limited, as long as the mechanical properties of the polyamide are not affected detrimentally. Usually the amount is between 10 and 1000 ppm copper, based on the total composition. Preferably 20 to 700, in particular 50 to 150 ppm copper are employed.

As organic halogen containing compound of the invention any aromatic and/or any aliphatic phosphate and/or any paraffin may be employed. Preferred are aromatic bromine containing compounds, bromine containing aliphatic phosphates and chlorine or bromine containing paraffins. The molecular weight of the employed compounds of the invention is not limited. It should be selected so that the compound is not too volatile, the compound can be mixed easily and homogeneously with the polyamide and shows only minor migration tendency in the final composition. Preferred are further bromine containing aromatic oligomeric epoxy resins, in particular compounds on the basis of tetrabromobisphenol-A.

Examples of usable paraffins are halogenated, in particular fluorinated, chlorinated or brominated paraffins. Usable are furthermore soft as well as hard paraffins. Preferred are compounds such as chloroparaffins (for example with an average formula of $\text{C}_{20}\text{H}_{24}\text{Cl}_{18}$), teflon waxes (for example with an average formula of $\text{C}_{20}\text{H}_{22}\text{F}_{20}$) and Viton copolymers (copolymers of hexafluoropropylene and vinylidene fluoride).

Examples of suitable compounds are:

Tris-(neobromopentyl)phosphate (phosphate 1), dibromodioxaphosphorinane derivatives and chlorine containing polyphosphonates and dekabromophenyl, dekabromophenylether, polydibromostyrene, tetrabromobisphenol-A, chlorinated and brominated styrene oligomers, tetrabromobisphenol-A-derivatives, such as BEB500C (EP-oligomer 1) and BEB6000 (EP-oligomer 2), which structures are given below, and chlorinated dimethanidibenzo(a,e)cacloocten-derivatives. Preferred are tris-(dibromoneopentyl)phosphate and dekabromophenyl and polydibromostyrene. It is furthermore possible to use mixtures of organic halogen containing compounds.

The addition amount of the halogen containing organic compound is usually below 10 wt.%. Typically such amounts are added so that 50 to 30,000 ppm halogen are present, preferably 100 to 10,000 ppm, more preferably 500 to 1500 ppm, based on the total composition.

Accordingly usually a ratio of copper to halogen in the stabilized polyamide compositions of from 1:1 to 1:3000 is obtained. Preferred is the area from 1:2 to 1:100, in particular the range from 1:5 to 1:15 (based on the molar ratio).

Higher addition amounts usually do not lead to an increase of the stabilization effect, polyamides containing more than 5% organic halogen containing compounds do have a significant lower stability. They show increased cleavage of polymer chains, which leads to premature embrittlement of the products and to strong discoloration. Preferably the content of organic halogen containing compound is less than 3 wt%, in particular less than 1 wt%.

The above defined copper salts and organic halogen containing compounds will be named stabilizer components in the following.

Polyamide compositions in accordance with the present invention show improved long term temperature stability, improved tracking resistance and lower discoloration. These advantages of the compositions of the present invention are deemed to be due to the synergistic effect of the organic halogen containing compounds, which must be added in minor amounts only.

The tracking resistance, which is determined as CTI-value is improved greatly with the use of the organic compounds. Accordingly the area of practice for the polyamide compositions in accordance with the invention is broadened to products which are used in the electro or electronic industry.

Polyamides for electrical products should possess CTI-values of 600, at least however of 550. This value is reached with pure polyamide. The CTI-value is determined in accordance with DIN-IEC 112.

The polyamide compositions in accordance with the present invention further show, compared with usual copper/halogen salt-stabilizers, improved electrical strength.

The used organic compounds show, compared with halogen salts an improved dispersion ability in the polymer melt. Therefore a complicated homogenisation can be omitted. If at the same time a copper salt such as copper stearate is employed, the stabilizer itself is meltable and therefore easy to disperse in the polyamide.

The stabilizing components are compatible with all sorts of polyamines. Therefore blooming at the processing apparatuses (nozzles, extruders, molds) and the produced parts and filaments does not occur.

Furthermore the polyamide compositions in accordance with the present invention do show only very limited tendency towards discoloration. In particular with fiberglass reinforced polyamides with conventional copper stabilizers discolorations were so strong that these compositions were only usable after black coloration. It is therefore surprising that this discoloration occurs with the polyamide compositions according to the present invention only to a minor extent, if at all. It is possible to obtain compositions colored with pigments without color deviations. Even TiO_2 colored compositions maintain the clear white color. This opens a new application field for colored polyamides in areas where improved long term thermal stability is required, so long only obtainable with common stabilizers having the drawback of strong discoloration.

The polyamide compositions in accordance with the present invention therefore have the advantage of improved long term temperature stability while being at the same time colorable with pigments, without the danger that the usual own discolorations alter the pigment coloration.

For coloration of the polyamide compositions in accordance with the present invention all common pigments are suitable, such as titanium dioxide, lead white, zinc white, lipone, antimony white, carbon black, iron black, mangan black, cobalt black, antimony black, lead chromate, mangan, zinc yellow, zinc green, cadmium red, cobalt blue, berlin blue, ultramarine, mangan violet, cadmium yellow, schweinfurt green, molybdenum orange, molybdenum red, chromium orange and chromium red, iron oxide red, chromoxide green, strontium yellow, chromoxide green, molybdenum blue, chalk, ocker, umbra, green soil, terra di sienna and graphite.

The polyamide compositions in accordance with the present invention are furthermore excellent concerning their stability regarding hydrolysis. They show improved long term stability under acidic and basic conditions, vis-à-vis salt solutions, glycol water mixtures and hot fats and oils and organic solvents. Accordingly, the usually recognised decrease of mechanical strength (impact strength, tensile strength) and the tendency towards embrittlement of the polyamides is drastically reduced and the long term durability enhanced. Compared with usually employed stabilizers, such as phenolic or amine compounds or common copper/halogen salt-stabilizers, improved effects are obtained.

The polyamide compositions in accordance with the present invention can furthermore be combined without limitations with further additives, such as lubricants, plasticizers, crystallization accelerators and pigments without detrimentally effecting the desired stabilization effect. In some cases even the used additives are stabilized against thermal decomposition or discoloration in polyamides. Therefore, polyamides mixed with plasticizers, such as BBS, or with waxes, such as montanates, no longer show a high tendency to ageing, when employed in polyamide compositions in accordance with the present invention.

Polyamides containing glass bowls, fiber glass, mineral additives or other reinforcing agents furthermore show, compared with common stabilizers, a significantly improved long-term thermal ageing stability.

The polyamide compositions in accordance with the present invention may contain furthermore usual fillers and reinforcing agents. Examples of suitable fillers and reinforcing agents are glass materials in the form of fibers, rovings, beads or powders,

oxidic materials, such as silics, alumina or aluminum silicates as well as graphite or plastic fibers or whiskers.

The above described advantages of the polyamide compositions of the present invention make it possible to use them for the preparation of fibers and for parts in the electric or electronic industry, mainly plug-in parts, plates (supports for electric contacts) and casing parts.

Furthermore, the stabilized polyamide compositions in accordance with the present invention were evaluated in order to determine whether any further improvement of the discoloration tendency could be achieved. Surprisingly, it was found that a further reduction of the discoloration could be achieved by the addition of organic phosphites or inorganic phosphonates or inorganic hypophosphites. These substances are known as color stabilizers in polyamides. It was, however, also known that these color stabilizers could lead often to the formation of copper oxides with copper salts. Therefore, a grey discoloration or brown/ black discolorations occurred. Therefore, it was surprising that the combination in accordance with the present invention does not lead to any discoloration and that, furthermore, the blue discoloration, occurring sometimes after conditioning could be reduced by the addition of organic phosphites or inorganic phosphonates or inorganic hypophosphites. The slight discoloration occurring during this mixing can be cross dyed for the preparation of color stable polyamides.

It was furthermore found that this addition furthermore retards the ageing of the polyamides during thermal storage. This effect is particularly significant with organic phosphites.

The employable organic phosphites are esters of the phosphoric acid. Employable are aliphatic as well as aromatic or mixed esters. Typical examples are, for example, dimethyl and diethyl phosphite, trimethyl and triethyl phosphite as well as the additives known in the plastic processing industry. Typical examples are Tris(2,4-di-t-butylphenyl)phosphite (Phosphite 20), Bis(2,4-di-t-butylphenyl)pentaerythritoldi-phosphite (Phosphite 21), Tetrakis(2,4-di-t-butylphenyl)4,4'-biphenylendiphosphonite (Phosphite 23), Distearylpentaerythritoldiphosphite, Diisooctylphosphite, Distearylphosphite, Triisodecylphosphite, Triisooctylphosphite, Trilaurylphosphite, Tristearylphosphite, Tris(dipropylenglycol)phosphite, Diphenylphosphite, Trisnonylphenylphosphite, Triphenylphosphite, Tris(p-nonylphenyl)phosphite. These compounds are available

under the tradenames Irgafos, Alkanox and Weston from the companies Ciba, Weston and The Great Lakes. Preferred are, in particular, Phosphite 20, Phosphite 21, Phosphite 22 and Phosphite 23.

Usable inorganic phosphonates are salts of the phosphonic acid. Employable as salt builders are alkali metals, earth alkali metals and all other usual metals. Preferred are, in particular, lithium, potassium, sodium, magnesium, calcium, strontium, barium and aluminum, in particular preferred are sodium, potassium, magnesium and calcium. A preferred phosphonate is disodium hydrogen phosphonate.

The usable inorganic hypophosphites are salts of the hypophosphoric acid. Concerning the salt building, it is referred to the above metals listed in connection with the inorganic phosphonates. The sodium salt of the hypophosphoric acid is a preferred example of the employable hypophosphites.

The addition amount of the above given additives is between 0.005 and 1.0% (50 to 10,000 ppm), preferably from 0.05 to 0.2% (500 to 2000 ppm) and in particular preferably from 0.075 to 0.15% (750 to 1500 ppm). These amounts relate everytime to the total composition.

The organic phosphites to be used are preferably melttable, processing stable and stable against extraction. This ensures that no phosphoric acid will be cleaved which may have disadvantageous effects for the total composition. The above given organic phosphites, in particular the Phosphites 20, 21, 22 and 23, satisfy the requirements excellently. Therefore, these compounds are particularly preferred.

It has, furthermore, been recognised during the preparation of the stabilized polyamide compositions in accordance with the present invention that the addition of the organic phosphite, the inorganic phosphonates and the inorganic hypophosphites should preferably occur only after the preparation of the basic composition stabilized with the stabilizing components.

If a stabilized polyamide composition in accordance with claim 1 is produced first and if the organic phosphite, the inorganic phosphonate or the inorganic hypophosphite is added only thereafter during an additional step, no discoloration occurs. The above described procedure is in particular effective with inorganic phosphonates. The organic

phosphite, the inorganic phosphonate or the inorganic hypophosphite can be added as such or in the form of a masterbatch. Concerning the masterbatch technology it is referred to the previous disclosure in this respect, the same principles are valid here. The production of the polyamide compositions is carried out usually by mixing at least one polyamide with at least one copper compound and at least one halogen containing compound, selected as defined in claim 1.

It is possible to mix the components using common apparatuses, namely polyamide and stabilizing compounds are mixed with one another and are fused. It is preferred, however, to first fuse the polyamide and to mix in subsequently the stabilizing components. It is even more preferred to add the stabilizing compound in the form of a master batch to the molten polyamide. This simplifies in particular the metering of the stabilizing components.

Suitable mixing apparatuses are known to the person skilled in the art and comprise mixing rollers, discontinuous kneaders, continuous extruders and kneaders and static mixers. Preferred is the use of continuous extruders, single screw extruders as well as double screw extruders, which allow a good mixing. Usually the polyamide will be fused in the extruder, the stabilizing component can be metered in later through suitable openings. This process as well as the apparatuses for these purposes are known to the person skilled in the art.

It is furthermore possible to add the stabilizing components during the production of the polyamides, for example by adding them to the monomer mixture. This leads to a very good dispersion without any further mixing step which reduces the production costs and the production time.

If a master batch of the stabilizing components is used for the production of the polyamide compositions in accordance with the present invention, the master batch can be produced in discontinuous mixers which allow a very good homogenous mixing, for example a Buss-kneader. However, usually continuous mixers are used such as double screw extruders or ZSK-extruders. The matrix material employed is usually the same polyamide which will be mixed later with the master batch. It is, however, also possible to use another polyamide or another polymer. The concentration of stabilizing components depends from the compatability of the matrix material and from the desired final concentration in the final blend and from good metering ability. Masterbatches with

concentrations up to 50% can be obtained, for example from a mixture of CuJ and polydibromostyrene (1:10).

In the following some preferred combinations of copper salts and organic halogen containing compounds are given.

Copper compound	Organic halogen compound
CuJ	Tris-(tribromoneopentyl)phosphate
CuJ	1,2,3-indioxaphosphorinane-5,5-bis(bromomethyl)-2-methoxy-2-oxide
CuJ	Polydibromostyrene
CuJ	Dekabromophenylether
CuCl ₂	Tris-(tribromoneopentyl)phosphate
Cu-acetate	Tris-(tribromoneopentyl)phosphate
Cu-acetate	Tris-(tribromoneopentyl)phosphate
Cu-acetate	EP oligomer 2
CuJ	EP oligomer 1
CuJ	Dechlorane plus
CuJ	Chloroparaffin av. C ₂₀ H ₂₄ Cl ₁₈
CuJ	Teflon wax av. C ₂₀ H ₂₂ F ₂₀
Cu (II) stearate	Phosphate 1

The Ep oligomers in particular possess high temperature stability. Furthermore their combinations with copper compounds are cheap.

Polydibromostyrene and EP oligomer 1 are suitable for the preparation of highly concentrated masterbatches. Masterbatches up to 50% of these compounds can be prepared.

EP oligomer 2 can only be introduced up to 10%. Due to a reaction of the EP-end groups with amino groups in the polyamide a strong increase of the viscosity is encountered. This chemical reaction however has the advantage that the dispersion and bonding in the final product is increased.

The following examples illustrate the invention.

The samples tested in the following examples have been prepared and tested as follows.

Preparation of samples

Stabilizer mixtures and Ca-stearate as lubricant are mixed with polyamide granules and melted in an extruder. The mixture is homogenized in the extruder and extruded continuously. Subsequently granules are formed. Cu concentration was always 100 ppm, halogen concentration 1000 ppm (0.1%) and Ca-stearate concentration 0.3%. After drying the granules were formed into test samples using an injection molding apparatus for measuring impact strength (DIN 53453) and bending strength (DIN 53452).

Heat ageing DIN 53497 and DIN 53446

The previously prepared test samples were put in an heat oven at 130, 150 and 165°C and were stored at these temperatures until measurements have fallen under 50% of the initial values. The period until this value was taken as halftime und is the value for the heat ageing stability of the polyamide. This value demonstrates the effect of the employed stabilizers. Since many polyamides age very rapidly without stabilization (24h at 150°C) a use of these materials without stabilization is often not possible.

Tracking resistance (CTI-values)

Test samples werde produced of a size of 3x5 cm (3mm thickness; injection molding) and tested in accordance with DIN-IEC 112.

Color determination

Discoloration of test samples was evaluated optically. In addition the color intensity was evaluated with the determination of the brightness (DIN 6174; DIN 5033, Part 1-7).

Example 1

Stabilization of PA 6 , heat ageing at 150°C. Comparision with other copper stabilizers, addition amount 100 ppm copper, 1000 ppm halogen. Measurement of impact strength until value decreases to 50% of initial value (half value measurement); measurement of tracking resintance (CTI-value); color after molding and after conditioning, color determination (CIE Lab values; DIN 6174).

Table 2

	Type	Composition	Halftime (h)	CTI-value	Discoloration after formation	Discoloration after conditioning
1	Comparison	PA 6 (natur)	24	600	colorless	Colorless
2	Comparison	CuJ/KJ	1100	450	colorless	Light green
3	Comparison	Cu-acetate/KBr	750	400	colorless	Light blue
4	Comparison	Cu-stearate/KJ	800	450	Yellow-ish	Blue green
5	Invention	CuJ/PDBS	850	525	yellowish	yellowish
6	Invention	CuJ/DBDP E	850	550	Yellowish	Blue green
7	Invention	CuJ/Phosphat 1	1200	550	colorless	Blue green
8	Invention	CuJ/Phosphate 2	900	550	yellowish	Blue green
9	Invention	CuJ/TBBA EP oligomer 1	900	550	colorless	Blue green
10	Invention	Cu-acetate/TBBA EP oligomer 2	800	525	colorless	Light blue
11	Invention	Cu(II) acetate/phosphate 1	1100	500	beige	ocker

12	Invention	CuCl ₂ / phosphate 1	1000	550	beige	ocker
13	Invention	CuCl/ phosphate 1	900	550	beige	Light blue
14	Invention	CuBr / phosphate 1	900	600	colorless	Light blue
15	Invention	CuCO ₃ / phosphate 1	800	600	colorless	Light blue
16	Invention	CuJ/ chloroparaff in	950	550	brown	Brown
17	Invention	CuBr/ dechlorane plus	900	600	beige	Light brown
18	Invention	Cu- stearate/ dechlorane plus	850	600	beige	Light brown

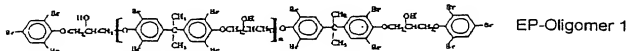
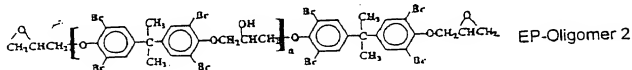
Table 2 (cont.)

after molding

after conditioning

Type	Discoloratio n	Brightness L-value	Discoloratio n	Brightness L-value	Green-red a-value	Blue-yellow b-value
1	Colorless	68.2	Colorless	69.3	-3.2	-1.8
2	Colorless	68.3	Light green	66.2	-11.7	4.2
3	Colorless	69.1	Light blue	68.2	-7.8	-1.5
4	Yellow-ish	67.5	Blue green	65.0	-7.7	2.9
5	Yellow-ish	68.8	Blue green	66.7	-9.6	-2.4
6	Yellow-ish	69.2	Blue green	68.7	-5.9	-3.2
7	Colorless	69.8	Blue green	69.2	-8.9	-1.8
8	Yellow-ish	67.3	Blue green	66.7	-5.6	6.9

9	Colorless	68.8	Blue green	68.3	-8.5	0.6
10	Colorless	69.2	Light blue	68.4	-8.8	4.0
11	Beige	61.78	Ocker	59.81	-4.5	4.6
12	Beige	63.47	Ocker	61.41	-4.4	2.6
13	Colorless	69.55	Light blue	67.08	-7.7	-2.1
14	Colorless	68.47	Light blue	57.71	-6.9	-2.4
15	Colorless	68.09	Light blue	67.32	-7.2	-2.0
16	Brown	22.99	Brown	22.61	2.6	6.9
17	Beige	46.42	Light brown	43.80	0.8	4.2
18	Beige	49.81	Light brown	47.36	-3.7	2.8

REF500C**REF600M**

These results show that the polyamide compositions, stabilized in accordance with the invention do show significantly improved tracking resistance and at the same time prolonged thermal stability. Discolorations are not detrimental for a later coloration of the samples of the invention.

Further experiments were carried out as above using 1000 ppm phosphite or phosphate. Samples and results are given in table 2a

Table 2a

	Type	Compositio n	Halftime (h)	value	Discolorati on after molding	Discolorati on after conditionin g
19	Invention	CuI/ phosphat 1/ phosphits (23)	1150	600	colorless	Light blue
20	Invention	(CuI/ Phosphate 1) in polyamide/ phosphite (20)	1100	600	Colorless	Light blue
21	Invention	(CuI/ PDBS) in polyamide/ phosphite (21)	1200	600	Colorless	Light blue
22	Invention	CuI/ PDBS) in polyamide/ disodium hydrogen phosphate	1100	550	Colorless	Light blue
23	Invention	Cu(II) stearate/ phosphate / phosphite (21)	900	600	colorless	Light blue

After molding

after conditioning

Type	Discoloration	Brightness L-value	Discoloration	Brightness L-value	Green-red a-value	Blue-yellow b-value
19	colorless	70.07	Light blue	68.21	-7.7	-2.8
20	Colorless	73.68	Light blue	71.78	-8.2	-3.3
21	Colorless	69.96	Light blue	67.95	-7.4	-2.7
22	Colorless	68.89	Light blue	66.21	-5.9	-1.0
23	colorless	68.32	Light blue	66.09	-6.3	-1.8

Example 2

Stabilization of PA 66 (natur), heat ageing test at 165°C, Compositions and measurements as in example 1. Additional experiments with 1000 ppm phosphite or phosphonate were done also.

Table 3

Type	Composition	Halftime (h)	CTI-value	Discoloration after formation	Discoloration after conditioning
Comparison	PA 66 (natur)	12	600	Colorless	colorless
Comparison	CuJ/KJ	140	450	Colorless	Light green
Comparison	Cu-acetate/KBr	90	400	Colorless	Light blue
Comparison	Cu-stearate/KJ	90	450	Yellowish	Blue green
Invention	CuJ/ PDBS	130	525	Yellowish	Blue green

Invention	CuJ/ DBDPE	130	550	Yellowish	Blue green
Invention	CuJ/ Phosphat 1	480	550	Colorless	Blue green
Invention	CuCl ₂ / phosphate 1	150	475	beige	brown
Invention	CuCl/ Phosphat 1	190	475	Colorless	Light blue
Invention	Cu-acatate/ Phosphat 1	350	475	beige	brown
Invention	Cu-acetate/	120	525	colorless	Light blue
Invention	CuJ/ EP- Oligomer 2	150	550	colorless	Blue green
Invention	CuJ/ dechlorane plus	330	550	beige	ocker
Invention	CuJ/ chloro paraffin	370	550	brown	brown
Invention	CuJ/ phosphate 1/ phosphite (20)	450	600	Colorless	Light blue
Invention	(CuJ/ PDBS) in polyamide/ phosphite (20)	450	600	Colorless	Light blue

Also these samples in accordance with the present invention do show improved tracking resistance and thermal stability so that the application of these samples in the electronic area is possible.

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Example 3

Stabilization of PA 66, reinforced with 30% fiberglass (GF30), experiments as in example 2. Halftime values relate to bending strength. Addition amount of phosphite or phosphate 1000ppm.

Table 4

Type	Composition	Halftime (h)	CTI-value	Discoloration after molding	Discoloration after conditioning
Comp.	PA 66 GF30	120	550	Colorless	Colorless
Comp.	CuJ/KJ	1200	450	Yellowish	Blue green
Comp.	Cu-acetate/ KBr	900	400	brown	Brown
Invention	CuJ/ PDBS	900	525	yellowish	Yellow green
Invention	CuJ/ phosphate 1	1800	525	Colorless	Yellowish
Invention	CuJ/ EP oligomer 1	1300	525	Colorless	Light green
Invention	CuJ/ Phosphate 1/ phosphite (2)	1300	550	Colorless	Light green
Invention	(CuJ/PDBS) in polyamide/ phosphite (21)	1400	550	Colorless	Light green

Samples in accordance with the invention do show, as in previous examples CTI-values allowing the use in electric parts.

Example 4

Stabilization of PA 66 (natur) and PA 66 GF30 with copper stabilizers, addition of 100 ppm copper, 1000 ppm halogen, 1000 ppm phosphite or phosphonate. Measurement of initial impact strengths: Izod with PA 66 (natur) and Charpy (not notched) with PA 66 GF30

Table 5

Type	Composition	Halftime at 165°C (h)	Impact strength (kJ/m ²)
Comp.	PA 66 GF30	120	45 (Charpy)
Comp.	CuJ/KJ	1200	35 (Charpy)
Invention	CuJ/ Phosphate 1	1800	41 (Charpy)
Comp.	PA 66 (natur)	12	5.5 (Izod notched)
Comp.	CuJ/KJ	140	4.0 (Izod notched)
Invention	CuJ/ Phosphate 1	480	5.5 (Izod notched)
Invention	CuJ/ Phosphate 1/ phosphite (20) in PA 66 GF30	1400	35 (Charpy)
Invention	(CuJ/ PDBS) in Polyamide 66/ phosphite (21)	1200	45 (Charpy)

Example 5

Extraction stability of PA 6 and PA 66 GF30 with water and ethanol. Evaluation in accordance with DIN 53738. Stabilization with 100 ppm copper and 1000 ppm halogen, 1000 ppm phosphite or phosphonate. Determination of extract composition after 16h reflux.

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Table 6

Type	Composition	Amount of extract (%)	Composition of extract
Invention/Water	PA 66 natur CuJ/ Phosphate 1	0.3	No copper or halogen or P
Invention/Water	CuJ/ Phosphate 1/ phosphite (21) PA66 natur	0.3	No copper or halogen or P
Invention/Water	CuJ/ Phosphate 1 PA66 GF30	0.2	No copper or halogen or P
Invention/Water	CuJ/ Phosphate 1/ Phosphite (21) PA 66 GF30	0.2	No copper or halogen or P
Invention/Ethanol	CuJ/ Phosphate 1/ PA6 natur	0.6	No copper or halogen or P
Invention/Ethanol	CuJ/ Phosphate 1/ phosphite (20) PA6 natur	0.6	No copper or halogen or P
Invention/Ethanol	CuJ/ PDBS /PA6 GF30	0.5	No copper or halogen or P
Invention/Ethanol	CuJ/ Phosphate 1/ phosphite (20)/ PA6 GF30	0.5	No copper or halogen or P

Example 6

Hydrolysis stability of PA 66 GF30, decrease of mechanical properties (hardness and bending strength) after storage in 100% glycol, 48h at 135°C. 150 ppm copper, 1500 ppm halogen, 1000 ppm phosphite or phosphonate.

Table 7

Type	composition	CTI-value	Ball-pressure hardness	Bending strength	Ball-pressure hardness (aS)	Bending strength (aS)
Comp.	CuJ/KJ/KBr	450	141	276	91	130
Invention	CuJ/ Phosphate 1	525	140	280	94	134
Invention	(CuJ/ PDBS) in polyimide/ Phosphite (21)	525	139	278	92	132
Invention	CuJ/ Phosphate 1 / Phosphite (20)	525	140	278	95	135

(aS): after storage, ball-pressure hardness measured in accordance with ISO 2039/1, bending strength measured in accordance with DIN 53456

Samples in accordance with the present invention and comparative examples show, that the polyamide compositions of the present invention show improved long term temperature stability and improved maximum temperature durability and improved tracking resistance. Also the tendency towards discoloration is reduced, compared with conventional polyamide compositions Initial impact strength is affected by use of stabilizers in form of salts (CuJ/KJ). Substitution of KJ with soluble costabilizers (phosphate 1) reduces the decrease significantly or even avoids it. This demonstrates the superiority of the samples of the invention.

Claims:

1. Stabilized polyamide composition, characterized in that as stabilizer at least one copper salt and at least one organic halogen containing compound are contained, wherein the organic halogen containing compound is selected amount the group consisting of:

- (a) aromatic compounds;
- (b) aliphatic phosphates; and
- (c) paraffins;

or mixtures thereof, with the proviso that, if the aromatic compound is a brominated styrene oligomer the polyamide is not polyamide 4.6.

2. Stabilized polyamide composition in accordance with claims 1, characterized in that the copper salt is selected among copper salts of organic and inorganic acids.
3. Stabilized polyamide composition in accordance with claims 1 or 2, characterized in that the copper salt is copper (I) halide.
4. Stabilized polyamide composition in accordance with at least one of the preceding claims, characterized in that the aliphatic phosphate is selected among tris-(tribromoneopentyl)phosphate, dibromodioxaphosphorinane derivatives and chlorine containing polyphosphonates.
5. Stabilized polyamide composition in accordance with at least one of claims 1 to 3, characterized in that the aromatic compound is selected among dekabromophenyl, dekabromophenylether, chlorinated dimethanodibenzo(a,e)-cyclooctenes, tetrabromobisphenol A, chlorinated or brominated styrene oligomers, tetrabromobisphenol A derivatives and polydibromostyrene.
6. Stabilized polyamide composition in accordance with at least one of claims 1 to 3, characterized in that the paraffin is chloroparaffin or bromoparaffin.

7. Method for the preparation of a stabilized polyamide composition, characterized in that at least one polyamide, at least one copper salt and at least one organic halogen-containing compound, selected among the group consisting of:
 - (a) aromatic compounds;
 - (b) aliphatic phosphates; and
 - (c) paraffins;

or mixtures thereof are mixed with one another, with the proviso that, if the aromatic compound is a brominated styrene oligomer the polyamide is not polyamide 4.6,

8. Process in accordance with claim 7, characterized in that the at least one copper salt and the at least one organic halogen containing compound are added in the form of a masterbatch.

9. Use of at least one copper salt and at least one organic halogen containing compound for the stabilization of polyamides, wherein the organic halogen containing compound is selected among the group consisting of:

- (a) aromatic compounds;
- (b) aliphatic phosphates; and
- (c) paraffins;

or mixtures thereof, with the proviso that, if the aromatic compound is a brominated styrene oligomer the polyamide is not polyamide 4.6.

10. Stabilized polyamide composition in accordance with at least one of claims 1 to 6, characterized in that further at least one organic phosphide, inorganic phosphonate or inorganic hypophosphite is contained.
11. Process for the preparation of a stabilized polyamide composition in accordance with claims 7 or 8, characterized in that in a further processing step at least one

organic phosphite, inorganic phosphonate or inorganic hypophosphite is added to the mixture obtained in accordance with claims 7 or 8.

Abstract

Stabilized polyamide composition, characterized in that as stabilizer at least one copper salt and at least one organic halogen containing compound are contained, wherein the organic halogen containing compound is selected amount the group consisting of:

- (d) aromatic compounds;
- (e) aliphatic phosphates; and
- (f) paraffins;

or mixtures thereof, with the proviso that, if the aromatic compound is a brominated styrene oligomer the polyamide is not polyamide 4.6.



Docket No.
14506

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**POLYAMIDE COMPOSITION, STABILIZED WITH
COPPER SALT AND AROMATIC HALOGEN COMPOUNDS**

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on October 15, 1999 as United States Application No. or PCT International
Application Number PCT/EP99/07848
and was amended on _____

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)		Priority Not Claimed
<u>198 47 626.4</u>	<u>Germany</u>	<u>15/October/1998</u>
(Number)	(Country)	(Day/Month/Year Filed)
_____	_____	_____
(Number)	(Country)	(Day/Month/Year Filed)
_____	_____	_____
(Number)	(Country)	(Day/Month/Year Filed)

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I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

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(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration numbers)

Richard L. Catania, Reg. No. 32,608;

Mark J. Cohen, Reg. No. 32,211;

Frank S. DiGiglio, Reg. No. 31,346;

Paul J. Esatto, Jr., Reg. No. 30,749;

Edward W. Grolz, Reg. No. 33,705;

Kenneth L. King, Reg. No. 24,273;

Leopold Presser, Reg. No. 19,827;

William C. Roch, Reg. No. 24,972;

John S. Sensay, Reg. No. 28,757;

Send Correspondence to:

SCULLY, SCOTT, MURPHY & PRESSER

480 Garden City Plaza

Garden City, New York 11530

Direct Telephone Calls to: (name and telephone number)

Edward W. Grolz (516) 742-4343

Full name of sole or first inventor	
<u>Klaus Titzschkan</u>	
Sole or first inventor's signature	Date
<i>Klaus Titzschkan</i>	<u>June 28th, 1981</u>
Residence	
<u>Lowensteinerstr. 45, D-71543 Wuestenrot, Germany</u> <i>DEX</i>	
Citizenship	
<u>German</u>	
Post Office Address	
<u>same as above</u>	

Full name of second inventor, if any	
Second inventor's signature	Date
Residence	
Citizenship	
Post Office Address	